A SPECTROSCOPIC STUDY OF THE TETRACYANOETHYLENE-HEXAMETHYLBENZENE COMPLEX

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1964

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
May, 1967

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ACKNOWLEDGMENT

I am deeply indebted to my adviser, Dr. J. Paul Devlin, for his guidance during the course of this investigation.

I also wish to express my appreciation to our scientific glass-blower, Mr. W. Adkins, who constructed and remodified the cold cells used in this investigation.

This study was made possible by financial support from the National Institutes of Health and the Oklahoma State University Research Foundation.

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CHAPTER I

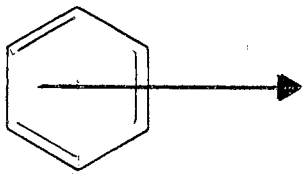
INTRODUCTION

The formation of a strongly colored complex from two colorless or nearly colorless organic compounds upon bringing them together is well known. The effect is generally attributed to an association of the original molecules in a definite ratio, most often 1:1, to form a new compound termed a "molecular complex" (1). In the past two decades or so, extensive experimental work has been done with a large group of complexes formed by the weak interaction of certain classes of organic substances, functioning as electron donors, with other substances which act as electron acceptors.

These donor-acceptor complexes, usually formed by integral mole ratios of the components, are in many cases so unstable that they cannot be isolated in the pure state at ordinary temperature but can exist only in solutions in equilibrium with their components (1). They can, however, usually be detected readily because of differences in their physical porperties (e.g., absorption spectra) from those of the pure components. The rates of formation of complexes in solution are generally so rapid that kinetic studies of the reactions are seldom possible by ordinary methods. The heats of reaction are generally small, and it is evident that the forces of coordination are much weaker than those established in the formation of covalent bonds. That is, the degree to which electron transfer from the donor to the acceptor components

takes place in much less than ordinarily occurs when new compounds are formed (1).

Alkenes, alkynes, aromatic hydrocarbons, and their substitution products can serve as donors and these are classified as π donors, that is, the electrons available for sharing are those residing in π molecular orbitals, and the adducts which they form are referred to as π-complexes. Formulas of type I and II are often used to describe the



electron transfer which takes place when a π donor coordinates with an acceptor (2).

Various organic compounds classified as dienophiles in the Diels-Alder reaction can serve as acceptors in interacting with unsaturated or aromatic compounds. Many of the so-called π-acid type acceptors are ethylenes which are substituted with highly electronegative substituents. The acceptor strength of such molecules is directly related to the capacity of these substituents to withdraw electrons from the ethylenic group. The exact nature of the coordination link between such complex components, however, has been the subject of extensive and controversial discussion over a long period of time. Pfeiffer considered the possibility that "residual valence forces" were saturated by the interaction. Bennett and Willis (4), on the other hand, proposed a covalent bond between the donors and acceptors. However, it is clearly established that the distances between the complexes are far longer than ordinary covalent bond lengths. Hammick and Yule (5) supported the view that

changes in the spectrum are associated with a transfer of electrons from one component to the other and suggested that the colors which accompany complex formation in solution result from such electronic interchanges between the components, when properly oriented, during normal collision. The term "contact charge transfer" has recently been applied in describing collisional electronic exchanges of this kind, and experimental evidence has been presented that in some instances the spectral changes which accompany donor-acceptor interaction in solution are partly collisional in origin and in part are characteristic of longer lasting association of the complex components. Weiss proposed that all molecular complexes have an essentially ionic structure B^+A^-, and pointed out that a low ionization potential for the base B, and a high electron affinity for the Lewis acid A, should then favor a stable complex. He attributed the color of molecular complexes to "intense charge-resonance spectra" arising within the ions of the complex (6).

Brackmann (7) attributed molecular complex formation to "complex resonance," meaning quantum mechanical resonance between a no-bond structure and a structure with a bond between the two parameters A and B, but made no clear statement about ionic character in the latter structure. He insisted that (assuming colorless partners) the complex as a whole determines the color, that is, that the light absorption causing color is not localized in one of the partners (7).

The Mulliken charge-transfer theory (1) in its simplest form assumes a wave function for the ground state of a weak complex of the form

$$\psi_N = a\psi_o(D,A) + b\psi_1(D^+-A^-)$$

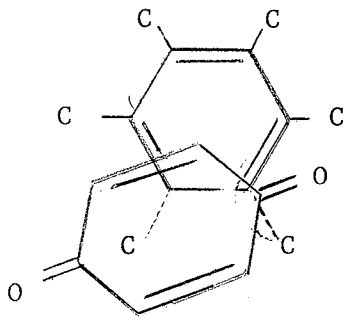
where ψ_o is the no-bond state, ψ_1 the dative state, a $\approx$1 and b is the dative coefficient with $a^2 \gg b^2$. In this popular theory a loosely bound molecular complex is regarded as a resonance hybrid receiving major conribution from a no-bond form and minor contribution from a dative form in which an electron has been transferred from the donor to the acceptor. The covalent bond of D^+-A^-, which might be described as an intermolecular semi-polar bond, is not necessarily interatomic in nature. In the case of the benzene iodine complexes, for example, the $C_6H_6^+I_2^-$ bond is considered to involve an electron in the π molecular orbital of $C_6H_6^+$ and an electron in a molecular orbital of I_2^-.

Studies of the geometries of donor-acceptor type complexes have been conducted on a number of complexes of aromatic π donors with aromatic or quinoid type π acceptors. In most cases the alternate stacking of donor and acceptor have been found. In some cases the donor and acceptor rings are stacked perpendicular to the line joining their centers; in other cases they are tipped out of this perpendicular arrangement. Generally the interplanar distances resemble those reported for graphite (3.4 Å) or crystalline polynuclear hydrocarbons. The forces of interaction in these crystalline complexes must, therefore, be relatively weak.

According to the Mulliken's concept of complex formation (1), interactions of aromatic donors and acceptors should be most favored if the rings are parallel and oriented with their centers directly over each other. Some shortening of the interplanar distance from the normal van der Waal's separation is also predicted as an accompaniment to the release of electrons from the donor to the acceptor. Deviations from this "ideal" configuration may result because of other factors which

influence structure only when the complexes are in the crystalline state.

In the hexamethylbenzene-chloranil complex, in which intercomponent hydrogen bonding does not occur, the donor and acceptor rings are apparently considerably less tilted out of a perpendicular orientation with respect to the line joining their centers than are the components of phenoquinone, (8) but the alternating rings differ in orientation by about 16^{o}.



The fact that the rings are not directly superimposed is attributed to the bulkiness of the methyl and chlorine substituents of the donor and the acceptor.

Tetracyanoethylene (TCNE) is well known as a strong π-acid and forms quite stable highly colored crystals when complexed with such donors as hexamethyl-benzene (HMB). These crystals are needle-like and seem to form from the alternate stacking of HMB and TCNE molecules such that all molecular planes are nearly perpendicular to the needle axis (3). Since TCNE was synthesized for the first time by Cairns et al., much attention has been directed to the π-complexes formed by TCNE with aromatic compounds.

The TCNE molecule belongs to the D_{2h} symmetry group. This implies that TCNE is a planar molecule similar in symmetry to ethylene. The

infrared spectrum of TCNE was first reported by Looney and Downing (17) who also gave the C ≡ N and C = C streching frequencies in the infrared and Raman spectra. They suspected that the molecular complexes should be regarded as products of electron donor-acceptor interaction.

The dichroic behavior of the activated bands in the infrared spectrum of the TCNE-HMB complex has been reported from this laboratory and interpreted in terms of Ferguson and Matsen charge oscillation theory. The most definite activation was found at 1562 cm^{-1} while the HMB band at 1380 cm^{-1} was greatly enhanced and shifted to 1390 cm^{-1}. A new band appeared at 2234 cm^{-1} but was somewhat hidden by the original TCNE activity. The activity at 1562 cm^{-1} was perpendicular to the molecular planes, that is, parallel to the needle axis, while most of the 1390 cm^{-1} activity was in-plane. Since the Raman line of the C = C streching mode is observed at 1569 cm^{-1} in pure TCNE, the 1562 cm^{-1} activity in the complex is assigned to this mode despite the perpendicular dipole. The 1380 cm^{-1} absorption in pure HMB results from out-of-phase methyl-group deformations so the expected activity is planar (3) but the strong enhancement was surprising.

In such oriented crystal studies the absolute band intensity calculation is not feasible because the sample thickness is not readily calculable. However, a method using a thin film technique in a cold cell enables one to measure the exact or nearly exact sample thickness, from which a fairly good degree of accuracy in the calculation of absolute intensities can be obtained.

This method has been used successfully by Hollenberg and Dows (9, 10). The method is based on the observation of interference fringes in the transmitted light as the sample is condensed in a thin film on

a substrate. The optical transmission of the cell and cold cell window is recorded as a function of time at a known fixed wave number while the compound to be studied is sublimed into the cell, where it condenses to form a solid film. The choice of silicon or some other infrared transparent material of high refractive index as a cell window is necessary. Since most molecular crystals have indices of refraction of roughly 1.5, they act as efficient antireflection coatings for silicon, (index of refraction of 3.6) giving intense fringes. If N is the number of fringes recorded and n_o the index of refraction of the sample at the observed wave number ν_o (in the near infrared region), then the sample thickness d is as follows:

$$d = \frac{N}{2N_o\nu_o}$$

The absolute intensities are calculable using the formula

$$B = \frac{1}{nd}\int_{band} \ln\left(\frac{T_o}{T}\right)d\nu$$

where n is the number of millimoles of sample per cubic centimeter, T and T_o are the transmissions with and without the sample, d is thickness, and ν is the frequency (wave number units). It was the objective of this research to employ the thin film method to obtain absolute intensities for several of the bands in the infrared spectrum of the HMB-TCNE complex, and to check the results against current theories on infrared intensities and the nature of the solid charge transfer complexes. The latter required that spectral intensities for pure HMB and pure TCNE be measured as well.

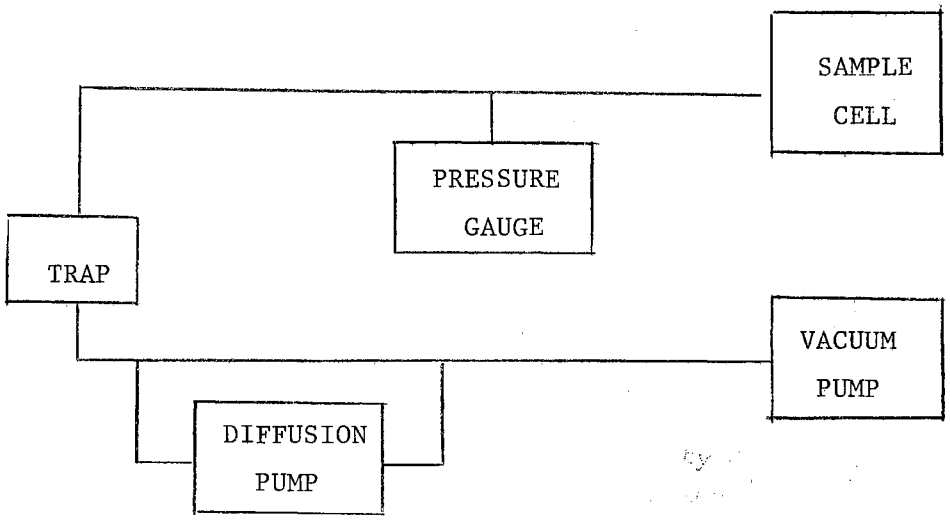
CHAPTER II

EXPERIMENTAL

APPARATUS

The low-temperature glass cell, which was constructed in this laboratory by our scientific glassblower, is compact, portable and cooled by liquid nitrogen. This cell is leak proof and can stand under a high vacuum. The sampling must be done under a high vacuum such that the cold sample will not be contaminated by condensation of other foreign substances, and the outer cell body remains reasonably warm and dry.

The entire vacuum system which consisted of a vacuum pump, a diffusion pump, a trap, a pressure gauge and the sample cell is shown below:



Since the sampling should be done under vacuum a high capacity vacuum pump is used to maintain 1 x 10^{-3} mm of mercury or better. This pump eliminates nearly all contaminants such as water, grease, and air from the sample cell within a couple of hours after the cell is assembled. The pressure range in which this pump operates is checked by a McLeod gauge attached to this system. An oil diffusion pump of standard construction is included in this system for this pump can lower the final pressure well below 1 x 10^{-3} mm of mercury. A liquid nitrogen trap is attached to this system in order to lower or to maintain the pressure, and to condense the contaminants which might decrease the efficiency of the pump. Since TCNE-HMB complex does not have an appreciable vapor pressure at room temperature it is required to heat the sample during deposition. A diagram of the cell is shown in figure I and the top view of this cell is given in Figure II. In order to volatilize the sample it is necessary to have a thermal connection between the sample source and the outside of tube A for it is thermally isolated by vacuum, and glass whose thermal conductivity is rather poor. Therefore, copper coil is inserted as shown in the diagram to satisfy this purpose and a heating tape is wrapped around tube A. A "Z" shaped copper valve is connected to the end of the sample compartment, and the nozzle of the valve is about 2 cm away from the center of the cell window, thus this gives an even deposition of the sample on the window, which in turn gives a good interference fringe pattern. This valve is made of copper because of the high thermal conductivity of copper for unless otherwise the sample might condense inside of the valve.

The sample compartment was made small enough to be heated all over and a pin hole was made through which the sample vapor could effuse,

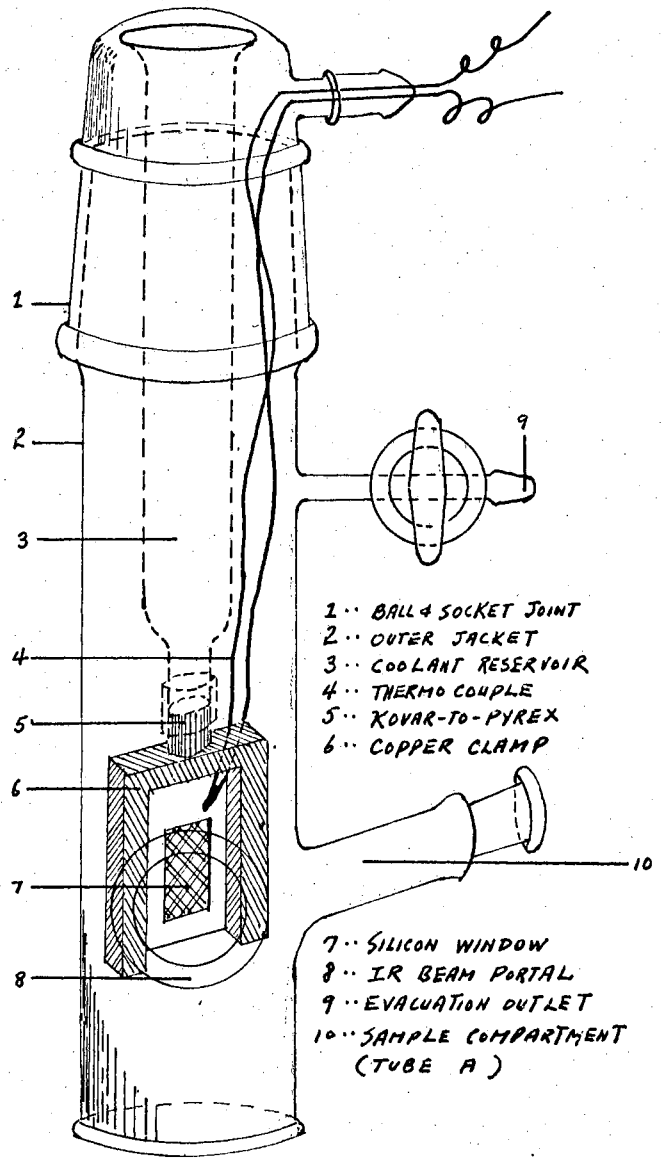


FIGURE I. LOW TEMP. INFRARED CELL

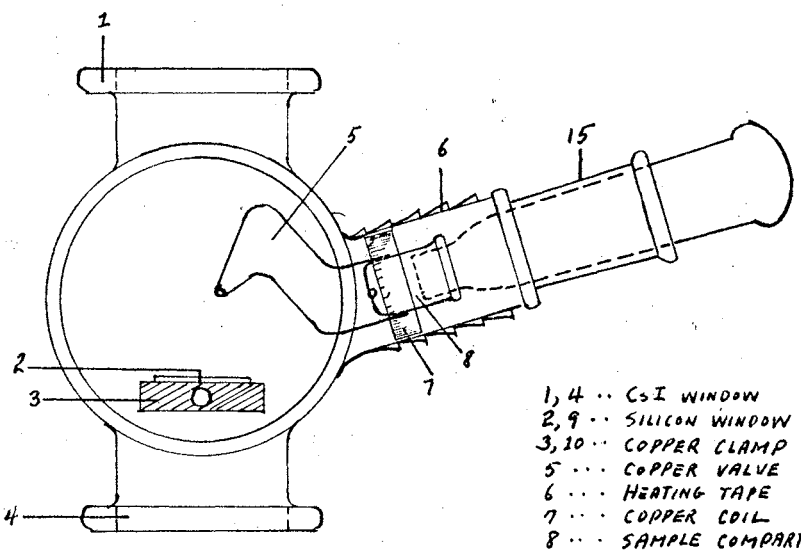


FIGURE II. COLD CELL - TOP VIEW

1, 4 .. CsI WINDOW
2, 9 .. SILICON WINDOW
3, 10 .. COPPER CLAMP
5 ... COPPER VALVE
6 ... HEATING TAPE
7 ... COPPER COIL
8 ... SAMPLE COMPARTMENT
11 .. KOVAR-TO-PYREX
12 ... COOLANT RESERVOIR
14 ... THERMOCOUPLE
15 ... TUBE A

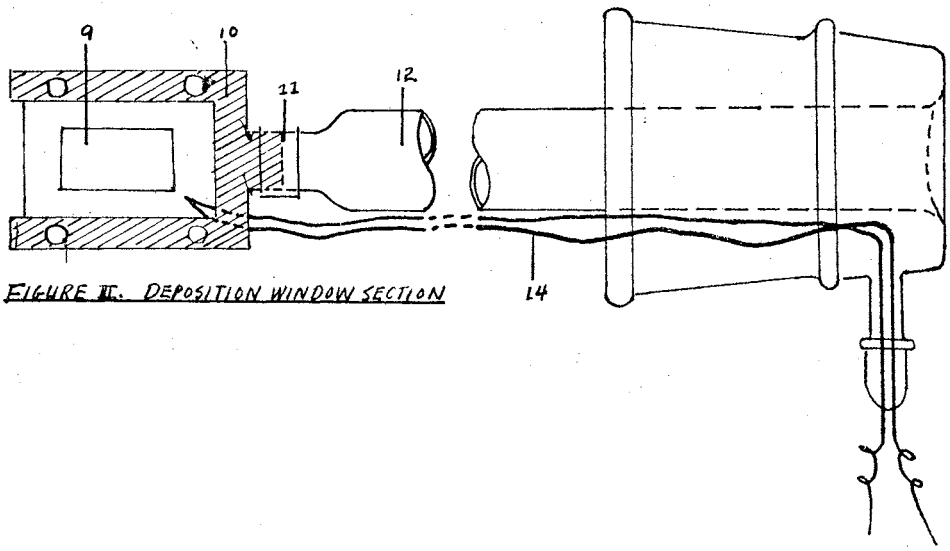


FIGURE III. DEPOSITION WINDOW SECTION

for the sample vapor scatters isotropically, condenses unless heated and slowly evaporates again during the experiment, introducing an error in the calculation of the sample thickness.

The deposition window is suspended on the dewar and can be rotated at any angle so that the spectrometer beam passes through the outside windows and hence through the deposited sample. The contact between the dewar and the deposition plate is made by Kovar-to-pyrex tube which ends in a forked clamp which holds the cell window. This clamp is made of copper so that the heat can conduct readily. The deposition window section is shown in Figure (III). In order to improve the thermal contact between the copper clamp and the cell window the addition of indium wire, as a gasket between them, has been necessary except when a silicon window is used whose thermal conductivity is itself sufficient. Apiezon greases, which have very low vapor pressures, were used in the glass joints and the flanged parts at which CsI windows are attached. The heating tape wrapped outside of tube A was connected to a powerstat set at 40 volts.

The entire system can be moved, thereby allowing the cold cell to be placed into the spectrometer sampling compartment while still under high vacuum and during deposition.

Sample Preparation

Crystals of TCNE-HMB complex have been grown by slowly evaporating ether solutions prepared from equimolar quantities of resublimed TCNE and the reagent grade HMB. The TCNE is resublimed from practical grade Eastman stock. Large, easily handled crystals are obtained from a modified sublimator. The HMB is pure enough to be used without further

purification. The TCNE-HMB complex appears to precipitate as closely packed parallel needle shaped crystals.

The cell components are cleaned by distilled water and acetone and then dried prior to assembling. Both sides of the silicon deposition window is polished to the degree of a mirror surface in order to minimize the surface scattering. For convenience, the cell is assembled in a humidity controlled room. The results show that atmospheric contamination is not a serious problem if a reasonable initial evacuation period is used (about one hour) while the pressure through the system is below 1×10^{-3} mm of mercury. The TCNE-HMB complex is contained in a tubular pyrex sample compartment (see figure II), which is heated through the copper coil by the heating tape connected to a powerstat.

About a 10 minute heating period prior to fringe scanning was used to let the sample attain an appreciable vapor pressure. Then the spectrometer chart drive is started with "scan" fixed at 4000 cm^{-1} to observe the interference fringes and deposition initiated by addition of liquid N_2 to the cell cold finger. It takes an hour to complete the deposition provided there is right amount of the sample (approximately 10 mg). By that time all the sample is completely evaporated as observed visually through the sample compartment for the TCNE-HMB complex is strongly purple-colored. Since interruption of the vaporization of the sample is not feasible in this system it is necessary to have an appropriate amount of the sample at the start. With too much sample there appears to be too many interference fringes with the later ones diffuse so that accurate sample thickness cannot be determined. An Iron-Constantan thermocouple is attached to this cell with one end fitted into the gap between the silicon window and the clamp. A standard

potentiometer is attached to the other end so that the window temperature may be recorded. The Z shaped copper valve, with one end a small nozzle was directed at about 45° toward the deposition window at a distance of about 2 cm from its center. It is necessary that the sample not deposit on the back side of the deposited window for it interferes with the interference fringe patterns. It is also necessary to have the rate of evaporation controlled so that all the sample goes to the front of the window and forms an even smooth film. When the rate is rapid the sample goes both to the back and front of the window and makes a rough film surface which scatters the infrared beam excessively. This phenomenon occurs when the powerstat is set at 60 or 70 volts. Further, it was found that the dry ice-in-acetone temperature is not sufficiently cold to permit sample deposition in a reasonable period of time. However, at a liquid nitrogen deposition temperature the crystals are in the form of a glass so that it is necessary to have the cold cell warmed to the dry ice-in-acetone temperature after deposition. At this temperature the glass form appears to change into regular crystal form. The change from the glass form to the one of the crystal seems to be gradual.

After the deposition was completed the heating tape was turned off, and a wavelength scan initiated while maintaining the temperature in the range of interest. After changing the coolant from liquid nitrogen to dry ice-in-acetone it takes more than an hour to have the form of the sample changed (from glass form to crystal form).

Infrared Sampling

A Beckman IR-7 infrared recording spectrophotometer was employed

for the investigation of all the samples which were prepared. This is a double-beam instrument designed for qualitative, quantitative and structural chemical analysis of liquid, solid and gaseous phase samples, capable of scanning from 200 to 4000 cm^{-1}. Quite high resolution is obtained by the fore-prism-grating optical system incorporated in the IR-7 monochromator. The region from 200 to 600 cm^{-1} is recorded using CsI prism-grating interchange in the monochromator and is referred to as the CsI region. The remaining region from 600 to 4000 cm^{-1} is scanned with the NaCl interchange. Since CsI is transparent over the region from 200 to 4000 cm^{-1}, as opposed to the lower limit of 600 cm^{-1} of NaCl, all the cells are sealed by means of thin CsI crystals. The reference cell is a standard 10 cm gas cell with CsI windows attached at both sides, which was periodically evacuated. One window of this cell was covered by a silicon platelet to compensate the absorption from the silicon window by the main cold cell. The sample cell has two outer CsI windows in addition to the silicon window on which the sample has been deposited. The loss of energy due to scattering was minimized by careful polishing of the CsI windows on a flat glass surface prior to each trial. The recording procedure is that which is commonly employed with this type of instrument. A recent modification which has been used effectively is the tracting accuracy control module which permits the sure precise positioning of strong absorption peaks. The scanning speed was set at 8 cm^{-1} per minute, and spectral slit width was set "selective" at 0.45 cm^{-1} at 4000 cm^{-1}.

After the degassing, but prior to sampling, a spectrum is obtained which represents the normal background due to the windows of the cell and general monochromator optics. This background absorption has been

removed from all of the spectra presented. The preparations at low temperature (liquid nitrogen temperature) were scanned while cold. Then the region between 1400 and 1500 cm^{-1} was scanned repeatedly during warm-up in order to detemine the temperature at which a doublet changed into a broad band. After the regular spectra were obtained the abscissa scale was quadrupled so that the integration of the band area would be easier. Recooled sample (liquid nitrogen from dry ice-in-acetone temperature) spectra were taken for the purpose of comparison.

Radiation from a mercury vapor lamp has been applied for more than two hours at liquid nitrogen temperature to check if the glass form would change to crystal form. No detectable annealing was achieved in this manner. Apparently the absorption of radiation energy of mercury vapor at this low temperature was not of the proper nature to change the glass to a crystal form in which the donor and acceptor molecules alternate in stacks.

CHAPTER III

RESULTS

Adapting the technique of measuring short optical path lengths by interference fringes to the problem of determining the thickness of a thin polycrystalline film of a molecular complex, so that the absolute intensities of the infrared absorption bands can be determined, has been emphasized in this experiment (9, 10).

This technique has proved to be the simplest and most generally applicable attack on the problem of measuring these intensities (11). Considerable time was spent mastering this technique. The samples used in this experiment were solids with low vapor pressure at room temperature, necessitating heating of the samples. These solid samples presented complications for designing the cold sampling cell. The main difficulty was in regulating the amount of sample at each trial. The data from preparations carried out at low temperature (liquid nitrogen temperature) will be described first.

All the sample films seemed to be uniform with a strong purple color for TCNE-HMB complex, and without colors for pure TCNE and HMB. When the rate of deposition was rapid the film surface appeared to be rough and the transmittance of the infrared beam was sharply reduced. At elevated temperature (-40^{o} or so) the purple color of TCNE-HMB complex changes to whitish-purple, and cuts the transmittance of the beam greatly. At room temperature all the sample films appear to be opaque.

These phenomena were checked by noticing the energy drop on the chart paper when scanning at a fixed frequency with the spectrometer. The film thickness ranged from 4μ to 12μ for this investigation, and give reasonable intensities for absolute measurements. The infrared spectra were studied in the range of 1100 to 1650 cm^{-1} and 2100 to 2300 cm^{-1} for TCNE-HMB complex from 1090 to 1225 cm^{-1} and 2100 to 2300 cm^{-1} for pure TCNE, and from 1300 to 1600 cm^{-1} for pure HMB.

At liquid nitrogen temperature the 1460 cm^{-1} bands from CH_3 wagging modes of HMB were split into two at 1440 cm^{-1} and at 1465 cm^{-1}. Upon increasing the temperature from liquid nitrogen to dry ice-in-acetone temperature these split bands gradually broaden merging into one peak while the peak at 1380 cm^{-1} shifts to 1390 cm^{-1} and is enhanced upon warming. The band at 1295 cm^{-1} irreversibly shrinks and almost disappears as the temperature goes up while the band at 1155 cm^{-1} grows. 1550 cm^{-1} band also shrinks irreversibly as the temperature increases. The relative intensities of the two peaks around 2250 cm^{-1} are reversed with increasing temperature.

Water vapor often interfered with this work, but was minimized by adjusting the balance control each time prior to using the instrument. The general shapes and band intensities agree with the work done by Stanley, et al. (3). The temperature at which the two bands at 1440 and 1465 cm^{-1} merge into one was not exactly detectable since the change was so gradual that there was more than 10^{o} deviation.

Absolute intensities in TCNE-HMB complex, TCNE, and HMB were calculated and are given in Table I. The most significant change with complexing is the fourfold increase in intensity of the 1380 cm^{-1} band.

TABLE I

ABSOLUTE INTENSITIES IN TCNE-HMB, TCNE AND HMB
ENTRIES ARE IN DARKS = cm mM^{-1}

Band	Compound and Sample Thickness					
	TCNE-HMB		TCNE		HMB	
	7.08μ	11.6μ	4.7μ	8.33μ	7.50μ	11.6μ
1150 cm^{-1}	863	850	1140	1140		
1380 cm^{-1}					1870	1700
1390 cm^{-1}	4070	3920				
1460 cm^{-1}	7480	7370			12400	12100

CHAPTER IV

DISCUSSION OF RESULTS

One observes generally three types of changes in the infrared spectra of conventional charge transfer complexes when compared with those of the pure isolated molecules which form the complexes: (1) the vibrational frequencies in donor or acceptor (or both) may be shifted, (2) modes may be activated or the intensities of the bands may be enhanced considerably, and (3) new low-frequency bands may appear because of the vibrations of one molecule in the complex against the other (12).

In this work the main emphases were put on the measurement of changes in the intensities of bands, with the intent of relating this to the amount of electron transferred from donor to acceptor upon formation of complexes.

The characteristic changes observed in the infrared spectrum of the bond stretching vibration upon formation of the complex are a decrease in its frequency and an increase in intensity whose magnitude depends upon the strength of the interaction between the electron donor and acceptor. Ferguson and Matsen (16, 19) have pointed out that intensity enhancement or activation of a mode can occur through an electron vibration mechanism. According to their mechanism, the electron affinity of the acceptor (or ionization potential of the donor) changes during certain vibrations. As a result, the energy difference

between the "no-bond" and "dative" states varies, so that the extent of mixing of these two wave functions changes during the vibration. Thus, the electron transferred from donor to acceptor in forming the dative structure may be thought to be vibrating back and forth between donor and acceptor. The resulting large change in dipole moment is responsible for the observed intensity enhancement.

Ferguson and Matsen's theory of weak complexes is based on the following model originated by Mulliken (1). The Mulliken charge-transfer theory which describes the donor-acceptor type molecular complex, is now generally accepted. Mulliken describes a 1:1 donor-acceptor complex in the ground state by assuming a wave function of this ground state of a weak complex of the form

$$\psi_N = a\psi_o(D,A) + b\psi_1(D^+-A^-)$$

Where ψ_o is the no-bond state, ψ_1 the dative state, $a \tilde{} 1$ and $a^2 >> b^2$.

If we neglect overlap, the dative coefficient b would be

$$b = \frac{H_{op}}{W}$$

where $H_{op} = \int \Phi_o H \Phi_p d\tau$, and W=I-(A+C); I, A and C are ionization potential of the donor, electron affinity of the acceptor and Coulomb energy term, respectively. The complex in the excited state E is described by

$$\psi_E \tilde{=} a^*\psi_1(D^+-A^-) - b^*\psi_o(D,A)$$

Here ψ_o is the wave function for the hypothetical "no-bond" structure (D-A) and ψ_1 is the "dative function" corresponding to the state with complete transfer of the electron ($D^+ - A^-$), and $a^* \simeq a$, $b^* \simeq b$ and $a^2 >> b^2$. The excited state, which presumably can be attained by the absorption of either visible or ultraviolet light, is largely dative

in character. The transition N → E which accompanies the absorption of light of appropriate wave length closely corresponds to the transfer of an electron from the donor to the acceptor. The corresponding spectrum of the complex, which is considered to be characteristic of the complex as a whole, is called an intermolecular charge transfer spectrum. The coordination products themselves are referred to by some authors as charge-transfer complexes.

If $\mu(D^+A^-)$ is defined to be the dipole moment of the dative state directed between the donor and acceptor, the equivalent dipole moment of the complex is given by

$$\mu_n = b^2 \mu (D^+A^-)$$

This relation requires that a change in dipole accompany a change in the value of (b).

Further, in terms of Q_i, a normal coordinate such as the c=c stretching mode, it follows that

$$\left(\frac{\partial b}{\partial Q_i}\right)_{Q_i = o} = 2b\mu (D^+A^-) \left(\frac{\partial b}{\partial Q_i}\right)_{Q_i = o}$$

Therefore if (b) changes with respect to Q_i this implies a variation in the dipole directed between the donor and acceptor. In particular a periodic variation of dative coefficient with donor or acceptor vibration will lead to a variation in dipole moment and consequently to infrared activity for that vibration in the charge-transfer complex. If the vibration is inactive or very weak in the non-complexed molecule, one observes an absorption or enhancement in the complex and such bands are observed in the infrared spectra.

By Mulliken's (1) theory of charge-transfer, (b) is directly related to the donor vertical ionization potential (I). Further, changes in the vertical ionization potential are functionally related to variations in scalar polarizability (P).

Therefore a relation exists among these parameters as following:

$$\mu_n \; \alpha b \; \alpha b(I) \; \alpha \; b \; (P).$$

in terms of normal coordinate Q_i, it becomes,

$$\left(\frac{\partial bn}{\partial Q_i}\right)_{Q_i=o} \alpha \left(\frac{\partial b}{\partial Q_i}\right)_{Q_i=o} \alpha \left(\frac{\partial P}{\partial Q_i}\right)_{Q_i=o}$$

Remembering that the first term of the above relation, $\left(\frac{\partial bn}{\partial Q_i}\right)_{Q_i=o}$ must be non-vanishing for infrared activity, it is sufficient, for infrared activation of Q_i, that the scalar polarizability change must be non-zero for the change in Q_i about $Q_i = 0$. Mathematically,

$$\left(\frac{\partial P}{\partial Q_i}\right)_{Q_i=o} \neq 0$$

This theory predicts that in a weak complex there can be infrared activation of the totally symmetric Raman fundamentals due to the variations in (b) caused by variations in the scalar polarizability. Ferguson and Matsen called this the "electron vibration" model since the electron would be pumped back and forth between the donor and acceptor with the frequency of the fundamental (16, 19). Depending on the geometric relationship between donor and acceptor molecules, the

electron vibration mechanism may give rise to an oscillating dipole perpendicular to the nuclear displacements i.e. in a sandwich type complex. The intensity (A_i) of the observed infrared band will be a function of the magnitude of the variation in (b) with variations in Q_i and therefore a function of the magnitude of

$$\left(\frac{\partial P}{\partial Q_i}\right)_{Q_i=o}$$

Mathematically this can be expressed by:

$$A_i \quad \alpha \left(\frac{\partial \mu n}{\partial Q_i}\right)^2_{Q_i=o} \qquad \alpha \qquad \left(\frac{\partial P}{\partial Q_i}\right)^2_{Q_i=o}$$

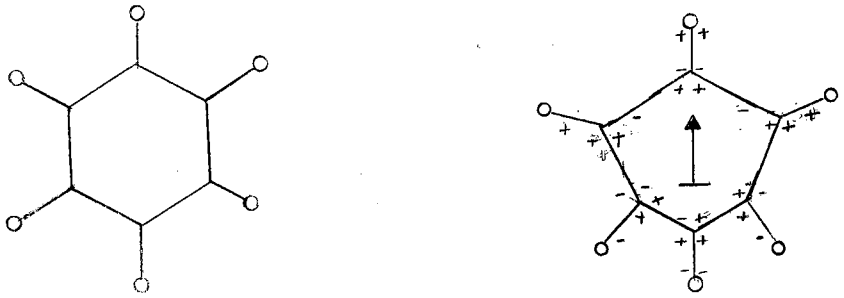
The 1560 cm^{-1} band arising from the perpendicularly oscillating dipole in the TCNE·HMB complex is quite consistent with this picture.

The normal vibrations of the free TCNE are observed in the spectra of aromatic complexes with little or no shift in position. However, in the TCNE·HMB complex new features of interest include the band appearing at 1560 cm^{-1} and the band at 1380 cm^{-1} which shifts to 1390 cm^{-1} and is greatly enhanced on the formation of TCNE·HMB complex. The new 1560 cm^{-1} band has been identified with the totally symmetric c=c streching mode active only in the Raman spectrum of the free TCNE molecules. Infrared polarization studies indicate that the oscillating dipole responsible for this absorption is oriented in the direction perpendicular to this TCNE molecular plane.

Thus in the sandwich TCNE-HMB complexes the activity of the modes which results from charge oscillation can in certain instances be related to the parameter $\frac{dP}{dQ_i}$. However, Brown's (15) recent theory emphasizes that enhancement or cancellation of activity in other modes

may result from a quite different source: changes in vibronic coupling accompanying charge transfer.

Brown (15) shows that the π electrons of a conjugated system will migrate as a result of variations in electron-electron repulsive forces during certain vibration. For example in a benzene ring the vibronic moment develops for the carbon-atom displacement as shown below. (The distortion is greatly exaggerated.)



(a) (b)

In this figure (a) shows the equilibrium configuration while in (b) the + and - signs indicate the polarization of the σ bond systems, relative to that in the equilibrium configuration. Qualitatively, the result can be understood in the following terms: electron-electron repulsions are increased at the end of the ring where the carbon-carbon distances decrease, and lessened where the carbon atoms move apart. There is, therefore, a migration of π-electron density to the end which is opening up. This migration produces a dipole which acts to cancel the bond moment dipole and thus reduces the infrared activity of this mode. In HMB it is similarly suggested that a vibronic moment develops in the e_1 methyl deformation mode as a result of the π-electron migration from one end, where three methyl groups are expanding, to the other

where three methyl groups are closing. The net effect is only weak activity in the 1380 cm^{-1} deformation mode. In a donor molecule, complex formation would reduce this effect through a decrease in the π-electron density. As this model would predict, therefore, the enhancement increases with acceptor strength (i.e., TCNE > chloranil > trinitrobenzene (3)). Thus, the fourfold increase in the activity noted in table I for this mode is attributed to just such a reduction in vibronic interaction. The absolute intensity of 1155 cm^{-1} band has not been changed significantly from pure TCNE to TCNE-HMB complex. Therefore, it is suggested that the c-c bond order in TCNE was not detectably affected upon formation of a complex in which electron clouds in HMB were shifted somewhat to TCNE while in an anionic TCNE the c-c bond order is slightly increased as a result of the radical anion. More obvious, however, is the failure of any vibronic coupling in TCNE to increase sufficiently to wash out infrared intensity in this mode as has been postulated for the anion (3).

Since the splitting of the CH_3 wagging modes of HMB at 1460 cm^{-1} does appear in the glass form as well as in the crystal form it is reasonable to presume that the doublet has been caused by intramolecular effects rather than crystal effects. The appearance of this splitting in the spectrum of the complex, wherein the HMB molecules are isolated between acceptor molecules, is itself suggests an intramolecular origin.

It is reasonable to consider the electrons, upon formation of a complex in the glass form where the donor and acceptor molecules do not equally alternate, as asymmetrically displaced thus causing a dipole moment which activates the HMB modes at 1295 cm^{-1}. This band irreversibly disappears upon formation of a crystal, implying that the

dipole moment oscillation is greatly reduced by symmetrical stacking of the molecules in the crystalline complex.

CHAPTER V

SUMMARY AND CONCLUSIONS

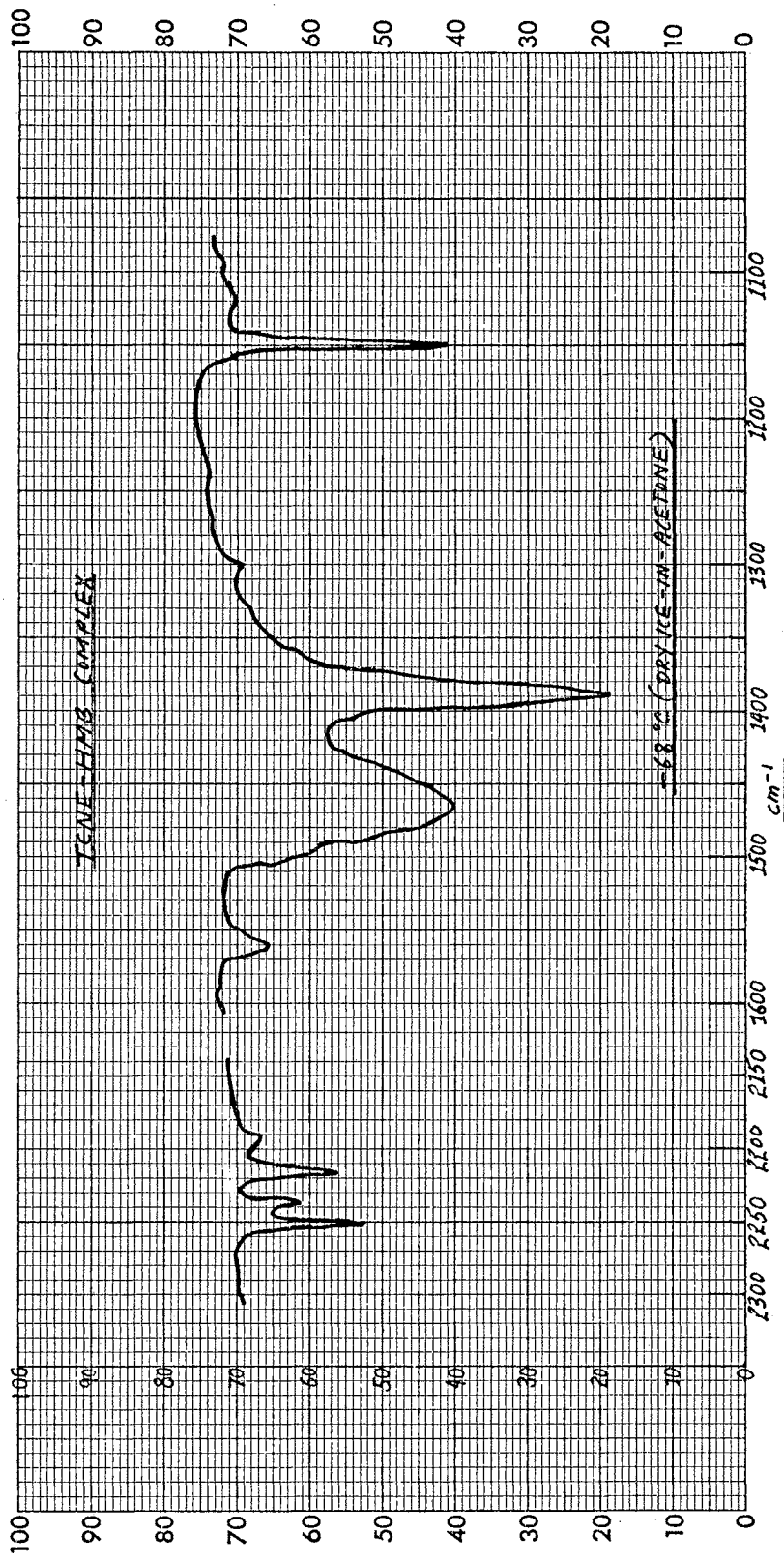
The primary purpose of this investigation was to measure the absolute intensities of TCNE-HMB complex, TCNE, and HMB from which one may be able to say something about the amount of electron density transferred from donor to acceptor molecule upon formation of a complex, and the effect of this transfer on vibronic interactions.

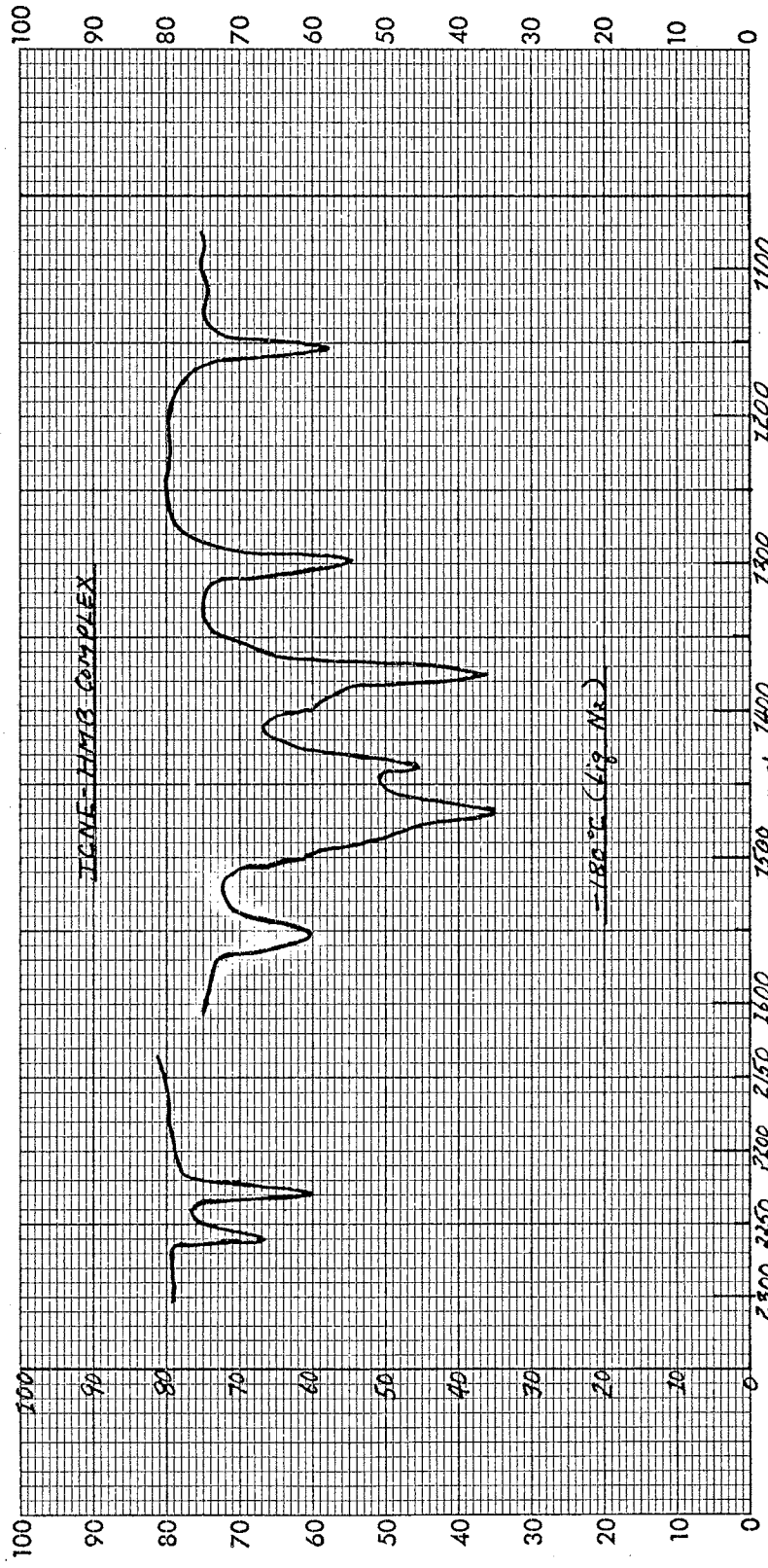
Infrared intensities are difficult to measure for there are many uncertainties introduced: (1) The path length is still difficult to measure. It is believed that the uncertainty in N (number of fringes) is significant when there are about 5 or less fringes. For intense bands, thin films (one or two fringes) are needed, so that the error in counting fringes are large. This error could be reduced somewhat by using shorter wave length to measure the film thickness, however, in a Beckman IR-7 the shortest wave length is 4000 cm^{-1}. (2) For thicker films, it is more difficult to count fringes, since the fringe intensity drops off, presumably because of a decrease in the quality of the film. (3) It is difficult to choose a base line for the integration in a meaningful and reproducible manner. (4) Densities of the molecules are not known exactly at such low temperatures as -180° C and -60° C. All these may add up to significant uncertainties in absolute intensity values in Table I. However, as far as relative intensities are concerned those numbers seem to be significant since the systematic errors

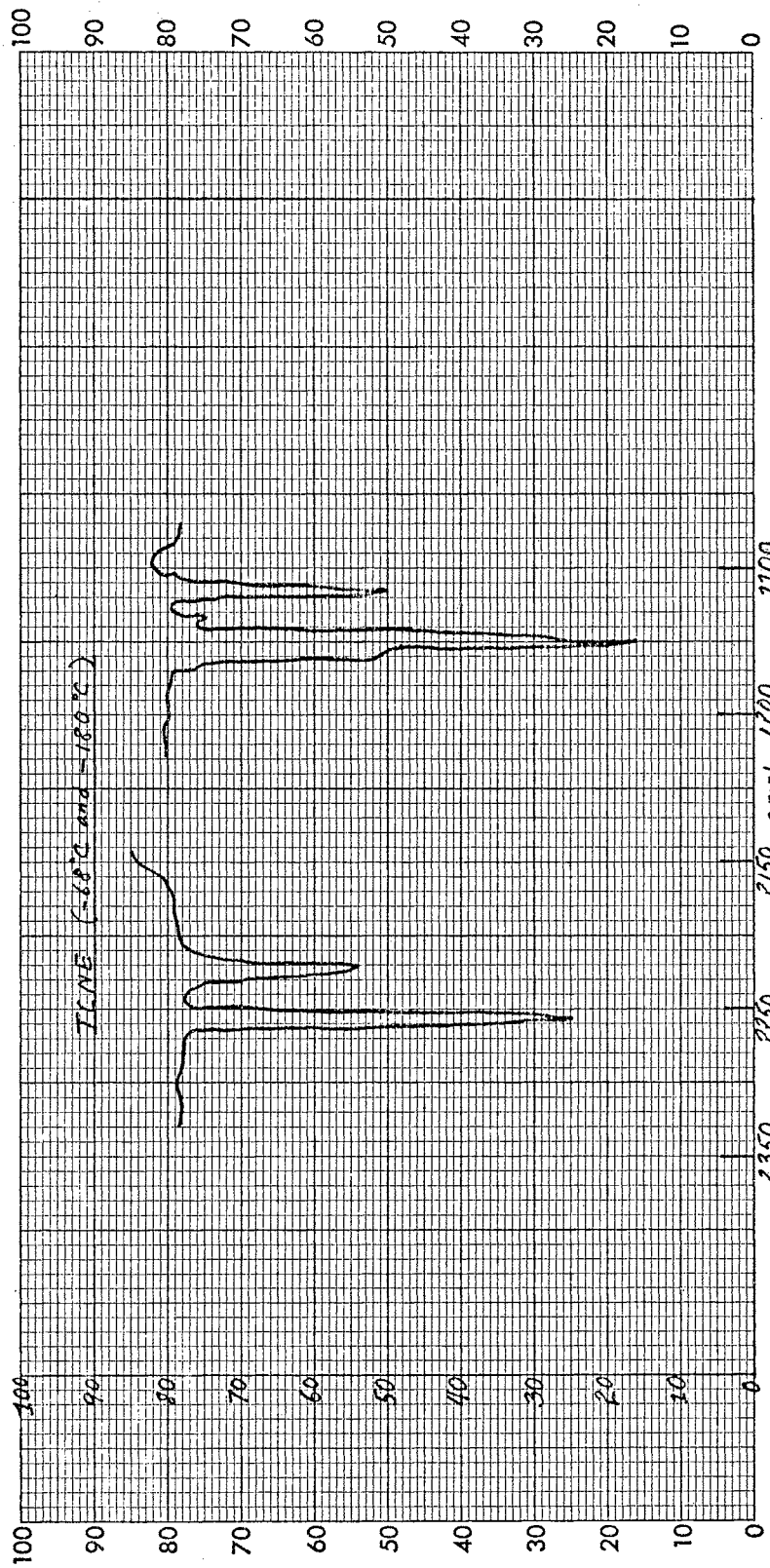
are cancelled out.

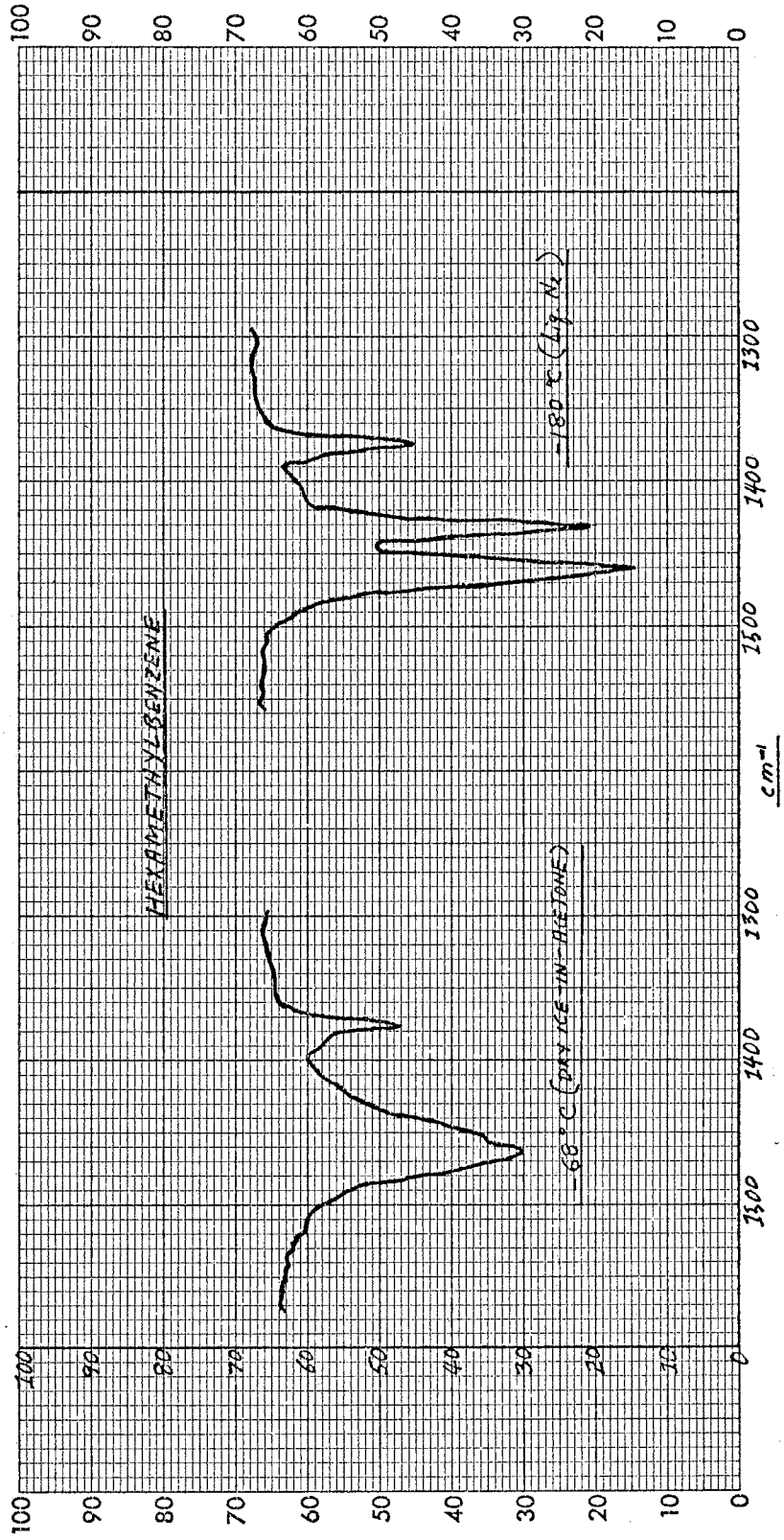
It is suggested that more refined techniques for measuring absolute intensities be developed, from which one may be able to correlate the absolute intensities with the quantum mechanical calculations for the electron transfer from donor to acceptor upon formation of a complex.

Finally, what has been done in this investigation is just a beginning. Methods have been tested for measuring film thickness from which one can calculate absolute intensities. However, the interference fringe technique seems to be the simplest and most generally applicable attack on the problem of measuring these intensities.


TCNE-HMB COMPLEX
-68°C (DRY ICE-IN-ACETONE)
cm-1
2300 2250 2200 2150 1600 1500 1400 1300 1200 1100


IRON-HMTA COMPLEX
—180°C (Liq. N2)
2300 2250 2200 2150 1600 1500 1400 1300 1200 1100
cm-1


100
90
80
70
60
50
40
30
20
10
0
1100
1200
2150
cm-1
2250
2350
TLNE (-68°C and -160°C)


HEXAMETHYLBENZENE
-180 °C (Liq. N2)
-68 °C (DRY ICE-IN-ACETONE)
cm-1
1300
1400
1500
1600
1700
100
90
80
70
60
50
40
30
20
10
0

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